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(54) Title: THERMOPLASTIC ELASTOMERS HAVING IMPROVED ADHESIVE PROPERTIES

(57) Abstract: Adhesive compositions comprising a thermoplastic elastomer and a block copolymer with rigid vinyl aromatic blocks and non-rigid blocks of dienes and vinyl aromatic monomers.

THERMOPLASTIC ELASTOMERS HAVING IMPROVED ADHESIVE PROPERTIES

BACKGROUND OF THE INVENTION

Field of the Invention

5 This invention relates generally to thermoplastic elastomer (TPE) materials. Thermoplastic elastomers are broadly defined as rubber-like materials that, unlike conventional vulcanized rubbers, can be processed and recycled like thermoplastic materials, yet have properties and performance similar to that of vulcanized rubber at service temperatures. The invention
10 more specifically relates to thermoplastic elastomers which have been modified by the addition of a specific vinyl aromatic block copolymer. The compositions of the invention have improved adhesive properties with respect to polymeric substrates, and particularly with respect to engineering thermoplastics.

15 Description of the Prior Art

 Blends which have a combination of both thermoplastic and elastic properties are generally obtained by combining a thermoplastic resin with an elastomeric material in a way such that the elastomer is intimately and uniformly dispersed as a discrete particulate phase within a continuous
20 phase of the thermoplastic. Early work with the vulcanization of the elastomer phase is found in U.S. Pat. No. 3,037,954 which discloses static vulcanization, as well as dynamic vulcanization wherein a vulcanizable elastomer is dispersed into a resinous thermoplastic polymer and the elastomer is cured (crosslinked) while continuously mixing and shearing the
25 blend.

 U.S. Pat. No. 4,130,535 discloses thermoplastic elastomer compositions comprising thermoplastic olefin resins and olefin copolymer

rubbers, prepared by dynamic vulcanization and wherein the rubber component is vulcanized to the extent that it is essentially insoluble in conventional rubber solvents. No details are given regarding adhesion properties of these compositions, but it is known that unmodified non-polar
5 thermoplastic elastomers generally do not adhere to engineering resins.

Efforts to improve the adhesive properties of thermoplastic elastomers have been made through the incorporation of functionalized thermoplastic resins into the blends. One approach is described in U.S. Pat. No. 4,957,968 which discloses the addition of a functionalized polyolefin to
10 improve adhesion to metals and polar polymers. U.S. Pat. No. 5,843,577 describes the incorporation of copolymers of polyamide and functionalized polyolefin to improve adhesion to polyamides. U.S. Pat. No. 5,852,118 discloses the addition of block copolymers of functionalized olefin, thermoplastic polyurethane, copolyester or copolyamide, and an isocyanate.
15 However, the problem of achieving good adhesion of thermoplastic elastomers to polymer substrates, and particularly to polar engineering thermoplastic substrates, either has not been overcome by these approaches or the techniques are too complex for practical application.

SUMMARY OF THE INVENTION

20 The present invention is based on the discovery that a thermoplastic elastomer composition having improved adhesion is provided by incorporating into the TPE a flexible block copolymer composed of blocks of vinyl aromatic monomers and blocks of dienes and vinyl aromatic monomers, and having a specific molecular structure. In detail the present invention
25 relates to a thermoplastic elastomer composition comprising
(a) from about 25 to about 90 weight percent of a thermoplastic elastomer;
(b) from about 10 to about 75 weight percent of a block copolymer of rigid blocks of vinyl aromatic monomers (S) and non-rigid blocks of dienes

and vinyl aromatic monomers (B/S) containing at least the block structure S-B/S-S, and wherein the diene content is less than about 40 weight percent of the total block copolymer and the non-rigid blocks B/S amount to at least about 50 weight percent of the total block copolymer.

- 5 The thermoplastic elastomer component (a) can be an olefinic thermoplastic elastomer wherein a thermoplastic olefin polymer and an olefin rubber are blended under conditions of heat and shear in the presence of a curative to at least partially vulcanize (crosslink) the rubber component to form a thermoplastic vulcanizate (TPV). The thermoplastic elastomer
- 10 component (a) can also be a styrenic block copolymer, or a mixture of olefinic and styrenic thermoplastic elastomers.

In a further embodiment of the invention thermoplastic polyurethanes can also be incorporated into the compositions.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

15 **Olefinic Thermoplastic Elastomer**

Thermoplastic Olefin Polymer Component

- Polyolefins suitable for use in the compositions of the invention include thermoplastic, crystalline polyolefin homopolymers and copolymers. They are desirably prepared from monoolefin monomers having 2 to 7
- 20 carbon atoms, such as ethylene, propylene, 1-butene, isobutylene, 1-pentene, 1-hexene, 1-octene, 3-methyl-1-pentene, 4-methyl-1-pentene, 5-methyl-1-hexene, mixtures thereof and copolymers thereof with (meth)acrylates and/or vinyl acetates. Preferred, however, are monomers having 3 to 6 carbon atoms, with propylene being most preferred. As used in
- 25 the specification and claims the term polypropylene includes homopolymers of propylene as well as reactor and/or random copolymers of propylene which can contain about 1 to about 30 weight percent of ethylene and/or an alpha-olefin comonomer of 4 to 16 carbon atoms, and mixtures thereof. The polypropylene can have different types of crystalline structure such as

isotactic or syndiotactic, and different degrees of crystallinity including materials with a high percentage of amorphous structure such as the "elastic" polypropylenes. Further polyolefins which can be used in the invention are high, low, linear-low and very low density polyethylenes, and copolymers of
5 ethylene with (meth)acrylates and/or vinyl acetates.

The polyolefins mentioned above can be made using conventional Ziegler/Natta catalyst systems or by single site catalyst systems. Commercially available polyolefins may be used in the practice of the invention.

10 The amount of thermoplastic polyolefin found to provide useful thermoplastic elastomer compositions is generally from about 8 to about 90 weight percent, with the proviso that the total amount of polyolefin and olefinic rubber is about 35 weight percent based on the total weight of the thermoplastic polyolefin, olefin rubber and optional additives. Preferably, the
15 thermoplastic polyolefin content will range from about 10 to about 60 percent by weight.

Olefin Rubber Component

Suitable monoolefin copolymer rubbers include non-polar, rubbery copolymers of two or more alpha-monoolefins, preferably copolymerized with
20 at least one polyene, usually a diene. Saturated monoolefin copolymer rubber, for example ethylene-propylene copolymer rubber (EPM) can be used. However, unsaturated monoolefin rubber such as EPDM rubber is more suitable. EPDM is a terpolymer of ethylene, propylene and a non-conjugated diene. Satisfactory non-conjugated dienes include
25 5-ethylidene-2-norbornene (ENB); 1,4-hexadiene; 5-methylene-2-norbornene (MNB); 1,6-octadiene; 5-methyl-1,4-hexadiene; 3,7-dimethyl-1,6-octadiene; 1,3-cyclopentadiene; 1,4-cyclohexadiene; dicyclopentadiene (DCPD); and vinyl norbornene (VNB).

Butyl rubbers are also useful in the thermoplastic elastomer compositions. As used in the specification and claims, the term butyl rubber includes copolymers of an isoolefin and a conjugated monoolefin, terpolymers of an isoolefin with or without a conjugated monoolefin, divinyl aromatic monomers and the halogenated derivatives of such copolymers and terpolymers. Another suitable copolymer within the scope of the olefin rubber of the present invention is a copolymer of a C_{4-7} isomonoolefin and a para-alkylstyrene, and preferably a halogenated derivative thereof. The amount of halogen in the copolymer, predominantly in the para-alkylstyrene, is from about 0.1 to about 10 weight percent. A preferred example is the brominated copolymer of isobutylene and para-methylstyrene. Natural rubbers are also olefin rubbers suitable for use in the thermoplastic elastomer composition.

The amount of olefin rubber in the thermoplastic elastomer generally ranges from about 70 to about 10 weight percent, with the proviso that the total amount of thermoplastic polyolefin and olefin rubber is at least about 35 weight percent, based on the weight of the polyolefin, rubber and optional additives. Preferably the olefin rubber content will be in the range of from about 50 to about 10 weight percent.

Additives

The thermoplastic elastomer may optionally contain reinforcing and non-reinforcing fillers, plasticizers, antioxidants, stabilizers, rubber processing oils, extender oils, lubricants, antiblocking agents, antistatic agents, waxes, foaming agents, pigments, flame retardants and other processing aids known in the rubber compounding art. Such additives may comprise up to about 65 weight percent, more preferably up to about 50 weight percent, of the total composition. Fillers and extenders which can be utilized include conventional inorganics such as calcium carbonate, clays,

silica, talc, titanium dioxide, carbon black and the like. The rubber processing oils generally are paraffinic, naphthenic or aromatic oils derived from petroleum fractions. The oils are selected from those ordinarily used in conjunction with the specific rubber or rubber component present in the composition.

Processing

The olefin rubber component of the olefinic thermoplastic elastomer is generally present as small, i.e. micro size, particles within a continuous polyolefin matrix, although a co-continuous morphology or a phase inversion is also possible depending upon the amount of rubber relative to thermoplastic resin and the degree of vulcanization, if any, of the rubber. Preferably, the rubber is at least partially vulcanized, and most preferably it is fully vulcanized (crosslinked).

The partial or full crosslinking can be achieved by adding an appropriate rubber curative to the blend of thermoplastic olefin polymer and olefin rubber, and vulcanizing the rubber to the desired degree under vulcanizing conditions. It is preferred that the rubber be crosslinked by the process of dynamic vulcanization. As used in the specification and claims, the term dynamic vulcanization means a vulcanization or crosslinking (curing) process wherein the rubber is vulcanized under conditions of shear at a temperature above the melting point of the polyolefin component.

Those of ordinary skill in the art will appreciate the appropriate quantities and types of vulcanizing agents, and the conditions required to achieve the desired vulcanization. Any known crosslinking system can be used, so long as it is suitable under the vulcanization conditions for the elastomer component and it is compatible with the thermoplastic olefin polymer component of the composition. Crosslinking (curing) agents include sulfur, sulfur donors, metal oxides, phenolic resin systems, maleimides,

peroxide based systems, hydrosilylation systems, high energy radiation and the like, both with and without accelerators and co-agents.

The terms fully vulcanized or completely vulcanized as used herein mean that the olefin rubber component of the composition has been crosslinked to a state in which the elastomeric properties of the crosslinked rubber are similar to those of the rubber in its conventional vulcanized state, apart from the thermoplastic elastomer composition. The degree of crosslinking (or cure) of the rubber can also be expressed in terms of gel content, crosslink density or amount of uncrosslinked rubber which is extractable by a rubber solvent. All of these descriptions are well known in the art.

Usually about 5 to about 20 parts by weight of the crosslinking agent or system are used per 100 parts by weight of the rubber component to be vulcanized.

15 **Styrenic Thermoplastic Elastomer**

Another thermoplastic elastomer useful in the invention is a block copolymer of styrene/conjugated diene/styrene, with the conjugated diene optionally being fully or partially hydrogenated, or mixtures thereof. Generally this block copolymer may contain about 10 to about 50 weight %, more preferably about 25 to about 35 weight %, of styrene and about 90 to about 50 weight %, more preferably about 75 to about 35 weight % of the conjugated diene, based on said block copolymer. Most preferred, however, is a block copolymer which contains about 30 weight % of styrene and about 70 weight % of the conjugated diene. The conjugated diene is selected from butadiene, isoprene or mixtures thereof. Specific block copolymers of the styrene/conjugated diene/styrene type are SBS, SIS, SIBS, SEBS and SEPS block copolymers. These block copolymers are known in the art and are commercially available.

Optionally the block copolymer may be further compounded with a polyolefin or a common additive or mixtures thereof. Thus, the styrenic thermoplastic elastomer optionally further comprises up to about 60 weight % of such polyolefin homopolymer or copolymer, or the additives or mixtures thereof, based on the total weight of the block copolymer and the polyolefin and/or additives. Preferably, the styrenic thermoplastic elastomer comprises at least 10 weight % of the polyolefin. The thermoplastic polyolefins are selected from those mentioned above in context with the olefinic thermoplastic elastomers.

The thermoplastic elastomer component of the invention may also be blends of the olefinic thermoplastic elastomer (comprising the polyolefin, rubber and optional additives) with the styrenic thermoplastic elastomer (comprising the block copolymer, optional polyolefin and/or additives). Preferred blends contain about 5 to about 95 weight % of olefinic thermoplastic elastomer and about 95 to about 5 weight % of styrenic thermoplastic elastomer respectively, based on the total weight of the thermoplastic elastomer component. These blends can be prepared by common blending processes known in the art.

The thermoplastic elastomer component of the compositions generally is present in an amount from about 25 to about 90 weight %, based on the total weight of thermoplastic elastomer and flexible block copolymer. Preferably it is present from about 25 to about 85 weight %, and most preferably from about 50 to about 75 weight %.

25 Thermoplastic Polyurethane

In a further embodiment of the invention, a thermoplastic polyurethane (TPU) can be included in the adhesive composition. The TPU component has no limitation with respect to its formulation other than the requirement

that it be thermoplastic in nature, which means that it is prepared from substantially difunctional ingredients, i.e. organic diisocyanates and components being substantially difunctional in active hydrogen containing groups. However, often minor proportions of ingredients with functionalities

5 higher than two may be employed. This is particularly true when using extenders such as glycerol, trimethylol propane, and the like. Any of the TPU materials known in the art can be employed within the scope of the present invention.

The preferred TPU is a polymer prepared from a mixture comprising at
10 least one organic diisocyanate, at least one polymeric diol and at least one difunctional extender. The TPU can be prepared by prepolymer, quasi-prepolymer or one-shot methods commonly used in the art.

The TPU component may be incorporated in amounts ranging from about 10 to about 50 weight %, and preferably from about 15 to about 35
15 weight %, based on the total of thermoplastic elastomer, TPU and flexible block copolymer.

Flexible Block Copolymer

The composition of the invention includes a flexible block copolymer component, which is comprised of a block copolymer containing rigid blocks
20 of vinyl aromatic monomers (S) and statistical non-rigid mid-blocks of diene/vinyl aromatic monomers (B/S). These block copolymers contain at least the block structure S-B/S-S. The glass transition temperature (T_g) of block S is generally above 25°C and that of the block B/S is generally below 25°C. The B/S block is composed of about 75 to 30 weight percent vinyl
25 aromatic monomer and about 25 to 70 weight percent diene monomer. Particularly preferred flexible B/S blocks have a vinyl aromatic monomer content of about 60 to 40 weight percent and a diene monomer content of

about 40 to 60 weight percent. With respect to the total block copolymer component the diene content is less than about 40 weight percent, preferably about 35 weight percent, and the portion of the non-rigid B/S blocks amounts to at least about 50 weight percent, preferably about 70
5 weight percent. The block copolymer component has a low modulus and yield strength, with high elongation.

Suitable vinyl aromatic monomers include styrene, alkyl-substituted styrenes such as p-methylstyrene, vinyltoluene, as well as mixtures of said monomers. The preferred monomer is styrene. Suitable diene monomers
10 include 1,3-butadiene, isoprene, piperylene, phenylbutadiene, and mixtures of said monomers. The preferred monomer is 1,3-butadiene. The conjugated diene monomer can also be fully or partially hydrogenated.

The block copolymers useful in the thermoplastic elastomer compositions of the invention are known in the art, and are further described
15 in Canadian Pat. No. 2,193,264 and in International Pat. Applications WO 96/20248; WO 96/23823; WO 98/12240; and WO 99/46330. They are generally prepared by butyl lithium initiated sequential anionic polymerization, but coupling of living S-B/S diblocks or bifunctional initiation are also known methods.

20 The amount of the block copolymer component in the composition of the invention generally ranges from about 10 to about 75 weight percent, based on the total weight of the composition including the thermoplastic elastomer component, additives and the flexible block copolymer component. The preferred amount of flexible block copolymer ranges from about 15 to
25 about 75 weight percent, with about 25 to about 50 weight percent being most preferred.

EXAMPLES

The following general procedure was used in the preparation of thermoplastic elastomers of the invention. The compositions were prepared

in a typical thermoplastic compounding twin screw extruder, although other conventional mixing devices such as Banbury mixers, Farrel continuous mixers and the like are also satisfactory. The pellets of block copolymer were preblended with the thermoplastic elastomer component, and the blend
5 was added to the extruder using a loss-in-weight belt feeder. The extrusion was set up to reach a melt temperature of at least about 180°C but not higher than about 220°C. One extruder vent was used as a vacuum port to remove trace volatiles and to prevent porosity in the extruded composition. The compositions were finished into spherical pellets using an underwater
10 pelletizer. After pelletizing, the compositions were molded into plaques for the determination of physical properties or were molded as described below for use in the peel test.

The compositions of the invention are rubbery materials having tensile set values of about 50% or less, which meet the standards for rubber as
15 defined by ASTM D1566. Preferred compositions have a Shore A hardness of about 65 or below and/or a tensile modulus (100%) of about 270 psi or lower.

The adhesive composition of the invention has unexpectedly improved adhesion to thermoplastic substrates such as terpolymers of acrylonitrile,
20 butadiene, and styrene (ABS), polycarbonate (PC), ABS/PC alloys and blends, polystyrene (PS), high impact polystyrene (HIPS), polyphenylene oxide (PPO), polymethyl methacrylate (PMMA), polybutylene terephthalate (PBT), polyethylene terephthalate (PET), acrylonitrile styrene acrylic (ASA), polypropylene, polyethylene and other olefinic polymers, including blends
25 and alloys of these polymers, as well as glass and mineral filled versions thereof. The compositions therefore can be used in processes for making shaped articles by conventional processes such as co-injection molding, co-extrusion molding, co-blow molding (injection and extrusion), lamination,

calendering, overmolding by compression and injection, insert molding, and over-extrusion. The shaped articles obtained by these processes are multilayer articles comprising at least one layer of a polymer substrate and at least one layer of the adhesive composition according to the invention. The adhesive composition and the molded and shaped articles made therefrom are useful in a variety of applications such as non-slip grips, soft touch labels and coatings, and consumer electronic, tool and appliance parts.

The following measurement methods were used in evaluating the examples of the invention:

- 10 Tensile strength at break; tensile set; tensile modulus; elongation at break - ASTM D412 (ISO 37, type 2)
 Shore hardness - ASTM D2240
 Tear strength - ASTM D624
 Specific gravity - ASTM D792
- 15 Adhesion of the compositions of the invention was measured by a peel test modeled after ASTM D 1876, with the modification that a hard and soft substrate was used in place of two soft substrates. Also, since adhesion is obtained at the substrate interface due to the inventive composition, no separate adhesive layer exists. For evaluation of insert molding conditions
- 20 the harder thermoplastic substrates were produced in an "L" shaped mold cavity, then were removed and allowed to cool to ambient temperature. The shaped plastic profile was then inserted into another mold with a "T" shaped cavity, so as to take up one-half of the cavity. The molten composition of the invention was then injection molded onto the existing "L" to produce a "T-bar"
- 25 article. For evaluation of compression molding conditions the thermoplastic "L" is produced as described, but is not removed from the mold. By either rotating the mold cavity to the next station or by using a sliding core plate, the molded "L" is immediately made accessible in a "T" cavity and the molten

composition of the invention is injected. A standard tensiometer was then used to measure peel values for the "T-bars", by placing each tab of the upper "T" in separate grips. The grips were then pulled apart at 180 degrees. The force to peel was plotted against the crosshead travel which is also the peel length down the profile. The curve typically reached a peak and then descended to a plateau. The plateau values were recorded as the adhesion, expressed as pounds per linear inch (pli).

The properties of compositions of the invention, and their adhesion to ABS and PC substrates are set forth in Tables 1 and 2

10

TABLE 1

Example No. -	1	2	3	4	5	6	7	8	9	10
Component (wt. %)										
SP8211-45W237								70	100	
SP9911-45W237	70	75	65	60	60	55	50			100
StyroflexBX6105	30	25	35	30	40	45	50	30		
Septon 4055				10						
Properties										
Hardness(ShoreA)	52	51	55	58	60	61	63	55	45	45
Tensile at break (psi)	580	540	610	930	920	1100	1210	610	475	500
Elongation at break (%)	590	590	640	710	740	770	780	540	500	450
Tensile modulus (100% (psi)	210	190	210	210	230	230	240	210	200	
Tensile set (%)	11	9	9	9	9	9	9		5	
Adhesion (pli)										
ABS (insert mold)	17	12	23	18	20	23	25	18	<1	<1
PC (insert mold)	28								<1	<1
ABS (compression mold)	26									
PC (compression mold)	37									

TABLE 2

Example No. -	11	12	13	14	15	16
Component (wt. %)						
SP8211-45W237	65	65	65	65	65	
Styroflex BX6105	35	25	17.5	25	17.5	35
Elastollan 1185		10	17.5			
Elastollan C85A				10	17.5	
Thermolast K - TC6AAZ						65
Adhesion (pli)						
ABS	19	16	7.5	20.5	17	8.5
PC	26.5	20	13	22.5	12	15

Adhesive compositions of the invention were prepared by blending 65 weight % SP8211-55W237 thermoplastic elastomer with 35 weight %

- 5 Styroflex BX6105 flexible block copolymer. Adhesion to various polymeric substrates was tested by the insert molding technique described earlier. Results of the peel strength tests are set forth in Table 3. In the description of the adhesion mode, the notation "cohesive" means that peel or failure occurred in the body of either the substrate or the thermoplastic elastomer of the invention. The notation "adhesive" means that the peel or failure occurred at the interface between the substrate and the thermoplastic elastomer of the invention.
- 10

TABLE 3

Substrate	Adhesion (pli)	Adhesion Mode
Polycarbonate (PC)	29	Cohesive
Acrylonitrile/butadiene/styrene (ABS)	21	Adhesive
PC/ABS blend	29	Cohesive
PC - 30% glass filled	23	Cohesive
Crystal polystyrene (PS)	29	Cohesive
High impact polystyrene (HIPS)	29	Cohesive
Polymethyl methacrylate (PMMA)	19	Adhesive
Acrylic styrene acrylonitrile (ASA)	15	Adhesive
ASA/PC	17	Adhesive
PC/polybutylene terephthalate (PBT)	21	Adhesive
Polyethylene terephthalate (PET)	17.5	Adhesive
Polypropylene (PP)	25	Cohesive
Polyphenylene oxide (PPO)	21	Cohesive

- 15 Abbreviations and product names used in the tables are defined as follows:

SP8211-45W237 - Santoprene® thermoplastic elastomer based on polypropylene and vulcanized EPDM rubber (Advanced Elastomer Systems, L.P.)

- 5 SP8211-55W237 - Santoprene® thermoplastic elastomer based on polypropylene and vulcanized EPDM rubber (Advanced Elastomer Systems, L.P.)

SP9911-45W237 - Santoprene® thermoplastic elastomer based on polypropylene and vulcanized EPDM rubber (Advanced Elastomer Systems, L.P.)

- 10 Styroflex® BX6105 - Flexible styrene-butadiene block copolymer (BASF Aktiengesellschaft)

Septon® 4055 - Thermoplastic elastomer SEPS block copolymer (Kuraray Co., Ltd.)

- 15 Elastollan® 1185 - Polyether based thermoplastic polyurethane (BASF Corp.)

Elastollan® C85A - Polyester based thermoplastic polyurethane (BASF Corp.)

Thermolast K™ - Compounded TPE based on SEBS (Gummiwerk Kralburg)

ABS - Acrylonitrile-butadiene-styrene terpolymer resin (Cyclocac® 5600 - GE)

- 20 PC - Polycarbonate resin (GE)

WHAT IS CLAIMED IS:

1. An adhesive composition comprising
 - (a) from about 25 to about 90 weight percent of a thermoplastic elastomer, and
 - 5 (b) from about 10 to about 75 weight percent of a block copolymer comprising rigid blocks of vinyl aromatic monomers (S) and non-rigid blocks of dienes and vinyl aromatic monomers (B/S) containing at least the block structure S-B/S-S, wherein the diene content is less than about 40 weight percent of the total block copolymer and the non-rigid blocks B/S amount to
 - 10 at least about 50 weight percent of the total block copolymer, based on the total weight of (a) + (b).
2. The composition of claim 1 further comprising from about 10 to about 50 weight percent of a thermoplastic polyurethane (c), based on the total weight of (a) + (b) + (c).
- 15 3. The composition of claim 1 wherein said thermoplastic elastomer (a) comprises a blend of thermoplastic olefin homopolymer or copolymer and olefin rubber, with optional additives.
4. The composition of claim 3 wherein said blend comprises a thermoplastic olefin polymer selected from the group consisting of polyethylene and
- 20 polypropylene, and an olefin rubber selected from the group consisting of ethylene-propylene copolymer rubber and ethylene-propylene-nonconjugated diene terpolymer rubber.
5. The composition of claim 3 wherein said olefin rubber is at least partially vulcanized.
- 25 6. The composition of claim 1 wherein said thermoplastic elastomer (a) comprises a styrenic block copolymer of styrene/conjugated diene/styrene.
7. The composition of claim 1 wherein said block copolymer (b) comprises rigid blocks of styrene and non-rigid blocks of 1,3-butadiene and styrene.

8. The composition of claim 1 wherein the glass transition temperature T_g of the rigid blocks of vinyl aromatic monomers is above about 25° C and the glass transition temperature T_g of the non-rigid blocks of dienes and vinyl aromatic monomers is below about 25° C.
- 5 9. The composition of claim 1 having a tensile set of about 50% or less as determined by ASTM D412.
10. An adhesive composition comprising
- (a) from about 50 to about 75 weight percent of a thermoplastic elastomer comprising a blend of polypropylene and dynamically vulcanized
- 10 ethylene- propylene-nonconjugated diene terpolymer rubber, and
- (b) from about 25 to about 50 weight percent of a block copolymer comprising rigid blocks of styrene and non-rigid blocks of 1,3-butadiene and styrene containing at least the block structure
- styrene-1,3-butadiene/styrene-styrene, wherein the 1,3-butadiene content is
- 15 less than about 40 weight percent of the total block copolymer and the non-rigid blocks amount to at least about 50 weight percent of the total block copolymer,
- based on the total weight of (a)+(b).
11. A shaped article comprising at least one layer of a thermoplastic
- 20 substrate which is at least partially in adherent contact with the composition of claim 1.
12. A method for the preparation of an adhesive composition, comprising the step of blending a thermoplastic elastomer with a block copolymer comprising rigid blocks of vinyl aromatic monomers (S) and non-rigid blocks
- 25 of dienes and vinyl aromatic monomers (B/S) containing at least the block structure S-B/S-S, wherein the diene content is less than about 40 weight

percent of the total block copolymer and the non-rigid blocks B/S amount to at least about 50 weight percent of the total block copolymer.

13. The method of claim 12 wherein said thermoplastic elastomer comprises a blend of thermoplastic olefin homopolymer or copolymer and olefin rubber,
5 with optional additives.

14. The method of claim 12 wherein said thermoplastic elastomer comprises a thermoplastic olefin polymer selected from the group consisting of polyethylene and polypropylene, and an olefin rubber selected from the group consisting of ethylene-propylene copolymer rubber and
10 ethylene-propylene-nonconjugated diene terpolymer rubber.

15. The method of claim 13 wherein the thermoplastic elastomer comprises a thermoplastic olefin matrix having dispersed therein discrete particles of olefin rubber which has been at least partially vulcanized by dynamic vulcanization.

15 16. The method of claim 12 wherein said thermoplastic elastomer comprises a styrenic block copolymer of styrene/conjugated diene/styrene.

17. The method of claim 12 wherein said block copolymer comprises rigid blocks of styrene and non-rigid blocks of 1,3-butadiene and styrene.

18. The method of claim 12 wherein the glass transition temperature T_g of
20 the rigid blocks of vinyl aromatic monomers is above about 25° C and the glass transition temperature T_g of the non-rigid blocks of dienes and vinyl aromatic monomers is below about 25° C.

INTERNATIONAL SEARCH REPORT

Intern. Application No.

PCT/US 01/02482

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08L23/10

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP 0 902 051 A (ASAHI) 17 March 1999 (1999-03-17) page 3, line 19 - page 8, line 45	1, 3-5, 7-15, 17, 18
Y	US 5 972 519 A (N. NIESSNER ET AL) 26 October 1999 (1999-10-26) column 2, line 20 - line 57 column 4, line 37 - line 58	1, 3-5, 7-15, 17, 18
A	DE 197 52 658 A (SUMITOMO) 4 June 1998 (1998-06-04) example 9	1-18

☐ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

* Special categories of cited documents:

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 O document referring to an oral disclosure, use, exhibition or other means
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 Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
 Z document member of the same patent family

Date of the actual completion of the international search

27 April 2001

Date of mailing of the international search report

28/06/2001

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No.

PCT/US 01/02482

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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